

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
24 March 2005 (24.03.2005)

PCT

(10) International Publication Number  
**WO 2005/026292 A1**

(51) International Patent Classification<sup>7</sup>: **C10G 2/00**

(21) International Application Number:  
PCT/EP2004/010635

(22) International Filing Date:  
17 September 2004 (17.09.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
MI2003A001777  
18 September 2003 (18.09.2003) IT

(71) Applicants (for all designated States except US): ENI S.p.A. [IT/IT]; Piazzale E. Mattei, 1, I-00144 Rome (IT). INSTITUT FRANCAIS DU PETROLE [FR/FR]; 1 et 4 avenue de Bois Préau, F-92852 Rueil-Malmaison (FR). ENITECNOLOGIE S.P.A. [IT/IT]; Via F. Maritano 26, I-20097 San Donato Milanese (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): MARETTO, Cristina [IT/IT]; Via Padre Granata 11, I-26900 Lodi (IT). PEDERZANI, Giovanni [IT/IT]; Via E. Fermi 12/B, I-20097 San Donato Milanese (IT).

(74) Agents: DE GREDORI, Antonella et al.; Ing. Barzano' & Zanardo Milano S.p.A., Via Borgonuovo 10, I-20121 Milan (IT).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE RUNNING OF A REACTOR SUITABLE FOR HETEROGENEOUS REACTIONS COMBINED WITH REACTIONS TAKING PLACE IN THREE-PHASE SYSTEMS

(57) Abstract: Process for the running of a reactor in which reactions take place in multiphase systems, wherein a gaseous phase prevalently consisting of CO and H<sub>2</sub> is bubbled into a suspension of a solid in the form of particles (catalyst) in a liquid (prevalently reaction product), according to the Fischer-Tropsch technology.



WO 2005/026292 A1

5

PROCESS FOR THE RUNNING OF A REACTOR SUITABLE FOR HETEROGENEOUS REACTIONS COMBINED WITH REACTIONS TAKING PLACE IN THREE-PHASE SYSTEMS

10       The present invention relates to a process for the running of a reactor suitable for heterogeneous reactions combined with reactions taking place in three-phase systems.

More specifically, the present invention relates to a  
15       process for the running of a reactor in which reactions take place in multiphase systems, wherein a gaseous phase, prevalently consisting of CO and H<sub>2</sub>, is bubbled into a suspension of a solid in the form of particles (catalyst) in a liquid (prevalently reaction product), according to the  
20       Fischer-Tropsch technology.

The Fischer-Tropsch technology is known in literature, for preparing hydrocarbons from mixtures of gas based on hydrogen and carbon monoxide, conventionally known as synthesis gas. A document which summarizes the main works on  
25       the Fischer-Tropsch synthesis reaction is represented by

Sie and Krishna, Appl. Catalysis A: General (1999), 186, 55-70.

The Fischer-Tropsch technology is typically based on the use of slurry reactors, reactors which are normally  
5 used in relation to chemical reactions which are carried out in multiphase systems in which a gaseous phase is bubbled into a suspension of a solid in a liquid. In the case of Fischer-Tropsch, the gaseous phase consists of synthesis gas, with a molar ratio  $H_2/CO$  ranging from 1 to 3, the liq-  
10 uid phase, at the reaction temperature, prevalently consists of the reaction product, i.e. essentially linear hydrocarbons with a high number of carbon atoms, and the solid phase is prevalently represented by the catalyst.

The Fischer-Tropsch reaction is an exothermic reaction  
15 which, for its industrial embodiment, requires internal heat exchanger devices, for removing the heat produced and for controlling the thermal profile inside the reactor.

The objective of the present invention is the running of the phases which are not included in the normal operating conditions for Fischer-Tropsch reactions and which are  
20 particularly critical for the catalyst performances, such as for example:

- charging;
- start-up/conditioning;
- 25 - make-up (subsequent additions of catalyst);

- temporary or definite shut-down of the reaction section;
- re-start-up after the temporary shut-down.

In scientific literature, for example in published  
5 Australian patent application AU 200066518 A1, a process is described for treating, in the charging phase, a catalyst for Fischer-Tropsch reactions which are carried in fluidized multiphase reactors and for running these during the shut-down or re-start-up phases.

10 The Applicants have now found an alternative process to that of the known art, for charging a catalyst into a bubble column slurry reactor and methods for the running of said reactor outside the normal operating conditions. The description of these methods is effected with the help of  
15 figure 1 enclosed.

The charging phase of a catalyst into a bubble column slurry reactor (B) at the moment of start-up, comprises:

- a) incorporating the catalyst, previously reduced in a matrix of paraffinic waxes, for example in the form of  
20 pellets, tablets or granules, solid at room temperature;
- b) melting and collecting the paraffinic matrix (1) in a vessel (A), maintained at a high temperature, together with a diluent (2) which is miscible with the  
25 molten paraffinic matrix and which is in liquid form

both under the conditions present in the container and at room temperature, a stream of inert gas (3) being distributed in said vessel (A) from the bottom so as to obtain a sufficiently homogeneous suspension;

5 c) pressurizing the vessel (A), in which the complete melting of the paraffinic matrix has been effected, at a pressure higher than that of the reactor (B) maintaining the system fluidized by the continuous  
10 introduction of inert gas from the bottom of said vessel;

d) transferring, due to the pressure change, the diluted solution (4) from the vessel (A) under pressure to the reactor (B), initially empty, maintained at a  
15 temperature higher than or equal to that present in the vessel (A) flushed in turn from the bottom with inert gas (5);

e) repeating steps (b) to (d) until a suspension level is reached in the reactor (B) which is sufficient for  
20 aligning the optional external equipment (E) envisaged for the treatment of the suspension (for example, degasifier, liquid-solid separators, pumps, etc.);

f) repeating steps (b) to (d) until the normal operating  
25 suspension level is reached in the reactor (B) and in

the optional external equipment (E) envisaged for the treatment of the suspension;

g) feeding the synthesis gas (6) diluted with an inert gas to the base of the reactor (B).

5 According to the present invention, the inert gas can consist, for example, of nitrogen or, preferably, purified natural gas.

In the present charging method, the catalyst is englobed in paraffinic waxes in the form of cylindrical blocks,  
10 wherein the quantity of wax ranges from 30 to 70% by weight. Any catalyst capable of being active in Fischer-Tropsch reactions can be used in the present process. The preferred catalyst is based on Co dispersed on a solid carrier consisting of at least one oxide selected from one or  
15 more of the following elements: Si, Ti, Al, Zr, Mg. Preferred carriers are silica, alumina or titania and their mixtures.

The cobalt is present in the catalyst in quantities ranging from 1 to 50% by weight, generally from 5 to 35%  
20 with respect to the total weight.

The catalyst can comprise further additional elements. It can comprise, for example, with respect to the total, from 0.05 to 5% by weight, preferably from 0.1 to 3%, of ruthenium and from 0.05 to 5% by weight, preferably from  
25 0.1 to 3%, of at least a third element selected from those

belonging to group 3 (IUPAC regulation). Catalysts of this type are known in literature and described, together with their preparation, in European patent 756,895.

Further examples of catalysts are again based on cobalt but containing tantalum, as promoter element, in quantities of 0.05-5% by weight, with respect to the total, preferably 0.1-3%. These catalysts are prepared by first depositing a cobalt salt on the inert carrier (silica or alumina), for example by means of the dry impregnation technique, followed by a calcination step and, optionally, a reduction and passivation step of the calcined product.

A derivative of tantalum (particularly tantalum alcoholates) is deposited on the catalytic precursor thus obtained, preferably with the wet impregnation technique followed by calcination and, optionally, reduction and passivation.

The catalyst, whatever its chemical composition may be, is used in the form of a finely subdivided powder having an average diameter of the granules ranging from 10 to 250  $\mu\text{m}$ .

The catalyst, englobed in the paraffinic matrix, is brought to a temperature higher than or equal to 150°C, for example, from 150 to 220°C, and diluted with a diluent liquid at those temperatures, and also at room temperature, for example with an oligomer of C<sub>6</sub>-C<sub>10</sub>  $\alpha$ -olefins, until a

concentration of solid ranging from 10 to 50% by weight is obtained. After the complete melting of the paraffinic matrix, the suspension is transferred into the reactor (B), maintained at a temperature higher than or equal to that of  
5 the melting vessel (A), by means of an internal heat exchanger. Under normal operating conditions, the exchanger serves for removing the reaction heat produced and maintaining the conditions more or less isothermal in the whole reaction volume.

10 During the transfer of the suspension, the reactor (B) is at a pressure lower than that present in the charging vessel (A) in order to favour the passage of the suspension from the vessel to the reactor due to the difference in pressure. The pressure in the charging vessel (A) is gener-  
15 ally higher than that present in the reactor (B) by about 0.2-0.4 MPa whereas the pressure inside the reactor is maintained at about 0.1-1 MPa. For the whole duration of the transfer process, a stream of inert gas (5) is maintained at the bottom of the reactor (B) to guarantee the  
20 suspension of the catalyst, thus preventing its sedimentation.

Both the temperature and pressure present inside the reactor (B) during the charging phase are lower than the values present during regime synthesis conditions. The  
25 Fischer-Tropsch reaction is in fact carried out at tempera-



tures equal to or higher than 150°C, for example ranging from 200 to 350°C, maintaining a pressure ranging from 0.5 to 5 MPa inside the reactor. More significant details on Fischer-Tropsch reactions are available in "Catalysis Science and Technology", vol. 1, Springer-Verlag, New York, 1981.

In order to reach the normal operating level inside the reactor (B) and all the optional apparatuses (E) envisaged for the treatment of the suspension, the melting, dilution and transfer from the charging vessel (A) to the reactor (B) are repeated various times. In relation to the concentration of the catalyst desired and plant production capacity, this operation can be repeated, for example, from 2 to 30 times.

During the first and subsequent charging steps, the reactor (B) is kept isolated from the optional equipment (E) envisaged for the treatment of the suspension, until an adequate suspension level is reached in the reactor itself enabling it to be on-line with said equipment (E). The charging steps are then completed until the normal operating level is reached. The vessels (A) and (B) have outlets (13) for the recovery of the vapour phase (inert gas and/or non-reacted synthesis gas, and/or synthesis reaction products in vapour phase under the reaction conditions).

At the end of the charging phase, before bringing the

system to the normal reaction and production conditions (14), a conditioning phase of the catalyst is activated. More specifically, at the end of the charging, the reactor (B) is in temperature conditions ranging from 150 to 220°C and a pressure ranging from 0.1 to 1 MPa, and is continuously fed with inert gas. The conditioning phase of the catalyst comprises:

- a) regulating the temperature and pressures at values suitable for the conditioning, i.e. within the range of 200-230°C and 0.5-1.5 MPa;
- b) gradually substituting the inert gas with synthesis gas, up to a concentration of inert gas ranging from 5 to 50% by volume and maintaining a partial water pressure (co-product of the Fischer-Tropsch synthesis reaction) lower than 1.0 MPa, preferably lower than 0.5 MPa, more preferably lower than 0.3 MPa;
- c) maintaining the conditions of point (b) for 24-72 hours;
- d) gradually increasing the pressure inside the reactor (B) up to regime values (0.5-5 MPa);
- e) gradually reducing the concentration of inert gas to zero until regime conditions; and
- f) gradually increasing the reaction temperature until reaching regime values (200-350°C).

Synthesis gas essentially consists of CO and H<sub>2</sub>, pos-

sibly mixed with CH<sub>4</sub>, CO<sub>2</sub> and inert gases in general; it has a H<sub>2</sub>/CO molar ratio ranging from 1 to 3 and preferably derives from steam reforming and/or partial oxidation of natural gas or other hydrocarbons, on the basis of the reactions described, for example, in U.S. patent 5,645,613. Alternatively, the synthesis gas can derive from other productions techniques such as, for example, autothermal reforming, C.P.O. (Catalytic Partial Oxidation) or from the gasification of coal with water vapour at a high temperature as described in "Catalysis Science and Technology", vol. 1, Springer-Verlag, New York, 1981.

When the reactor (B) is under regime conditions, periodic make-up of the catalyst is envisaged for compensating losses (in activity and material) during the overall production cycle, for example due to purges effected in the liquid-solid separation section.

In order to carry out the make-up of the catalyst, it is not only necessary to effect the melting of the pellets and their possible dilution with a solvent, but it is also preferable to proceed with the conditioning of the fresh catalyst before introducing it into the reaction environment. There is therefore a specific melting and conditioning section for this function, described in the enclosed claims, which is essentially based on:

- a vessel (C), equipped with an inlet for inert gas

(3'), where the pellets of catalyst, after the addition of a solvent (8), are charged (7) and melted, similar to that adopted for the initial charging, preferably having smaller dimensions, which is run under the same conditions as those of the main charging vessel (A);

- a reaction vessel (D), equipped with inlets for inert gas (5') and synthesis gas (6'), where the suspension is transferred (9) after melting, in which the catalyst undergoes the same conditioning process envisaged for the fresh catalyst used during the initial charging; said vessel (D) is designed for reaching higher pressures than those of the reactor (B) during normal operating conditions; after completing the conditioning procedure, in fact, the suspension is transferred (10) from the reaction vessel (D) to the main reactor (B) as a result of the pressure change.

The vessels (C) and (D) have outlets (13') for recovering the vapour phase (inert gas and/or non-reacted synthesis gas, and/or products of the synthesis reaction in vapour phase under the reaction conditions).

At the end of the conditioning phase of the catalyst and once the synthesis reactor (B) has been brought to regime conditions, the running of the latter can comprise a further two steps: stoppage (or shut down), with consequent

re-start-up, and a temporary stoppage phase, better known as stand-by.

The shut-down of a reactor (B) in which reactions are effected which take place in multiphase systems, wherein a gaseous phase, prevalently consisting of CO and H<sub>2</sub>, is bubbled into a suspension of a solid in the form of particles (catalyst) in a liquid (prevalently reaction product), requires the following operating phases:

- i. gradual stoppage of the feeding of synthesis gas (6) and its gradual substitution with inert gas (5);
- ii. possible reduction of the operating pressure and temperature inside the reactor (B) to values close to those of the conditioning phase;
- iii. discharging (4) of the suspension contained in the reactor (B) and (11) in the units associated therewith (E) and its recovery in the vessel (A) heated and flushed with inert gas (3); the transfer is effected by means of the difference in pressure, the vessel (A) having been previously brought to a pressure at least 3 bars lower than the reactor (B).

According to the present invention, the inert gas can consist, for example, of nitrogen or, preferably, of purified natural gas.

In this embodiment of the present invention, once the suspension has been discharged from the reactor (B) and

from the equipment (E) envisaged for the treatment of the suspension, such as degassing vessels and/or decanters and/or filters and other apparatuses such as recirculation pumps, and once the actions required for the shutdown phase  
5 have been completed, the reactor can be reactivated following the method described above, for example, for the charging phase.

The vessel (A) is designed to have a capacity which is such as to contain the volume of suspension present in the  
10 reactor (B) and in the other units (E), associated with the treatment of the suspension, at the moment of shut-down.

Should it not be necessary to empty the reactor (B) in the shut-down phase, in the case for example of a temporary stand-by phase, the latter comprises:

- 15 1. gradual stoppage of the feeding of the synthesis gas (6) and gradual substitution with inert and/or reducing gas, for example hydrogen (5) to keep the solid phase sufficiently dispersed in the suspension, at the same time minimizing any possible deactivation  
20 phenomena;
2. possible reduction in the operating temperature and pressure to values close to those of the conditioning phase.

In this phase, the reactor (B) can be kept in line  
25 with the treatment section of the suspension (E) which is

completely recycled, (11) and (12), to the reactor without the extraction of products. Alternatively, the reactor can be taken off-line from the units (E) after removing the suspension from the equipment (E) directly connected to the  
5 reactor (B). The latter is preferably designed to have a capacity which is such as to also contain the volume of suspension present in the units (E) at the moment of temporary stand-by.

10

15

20

25

CLAIMS

1. A process for the make-up of a catalyst in a reactor suitable for reactions which take place in three-phase systems according to the Fischer-Tropsch technique, to compensate losses (in activity and material) during the overall  
5 production cycle, which comprises:

- a) incorporating the catalyst, previously reduced in a matrix of paraffinic waxes, solid at room temperature;
- b) melting and collecting the paraffinic matrix (7) in a  
10 vessel (C), maintained at a high temperature, together with a diluent (8) which is miscible with the molten paraffinic matrix and which is in liquid form both under the conditions present in the vessel and at room temperature, a stream of inert gas (3') being distributed in said vessel (C) from the bottom so as to obtain a sufficiently homogeneous suspension;
- c) pressurizing the vessel (C) in which the complete melting of the paraffinic matrix has been effected at a pressure higher than that of the conditioning reactor (D) maintaining the system fluidized by the continuous introduction of inert gas (3') from the bottom  
20 of said vessel (C);
- d) transferring, due to the pressure change, the diluted solution (9) from the vessel (C) under pressure to the  
25 reactor (D), initially empty, maintained at a tempera-



ture higher than or equal to that present in the vessel (C) and flushed in turn from the bottom with inert gas (5');;

- e) regulating the temperature and pressure in the reactor (D) at values ranging from 200-230°C and 0.5-1.5 MPa;
  - f) gradually substituting the inert gas (5') with synthesis gas (6') up to a concentration of inert gas ranging from 5 to 50% by volume and maintaining a partial water pressure (co-product of the Fischer-Tropsch synthesis reaction) lower than 1.0 MPa;
  - g) maintaining the conditions of point (f) for 24-72 hours;
  - h) gradually increasing the pressure inside the reactor (D) to a value higher than the pressure of the reactor (B);
  - i) gradually reducing the concentration of inert gas to zero;
  - j) gradually increasing the reaction temperature until reaching values ranging from 200 to 350°C;
  - k) after completing the conditioning phase, transferring (10) the suspension from the reaction vessel (D) to the main reactor (B), which is running under normal operating conditions, by means of a pressure change.
2. The process according to claim 1, wherein the catalyst is englobed in paraffinic waxes in the form of pellets

wherein the quantity of wax ranges from 30 to 70% by weight.

3. The process according to claim 1 or 2, wherein the catalyst comprises Co dispersed on a solid carrier consisting of at least one oxide selected from one or more of the following elements: Si, Ti, Al, Zr, Mg and their mixtures.

4. The process according to claim 3, wherein the cobalt is present in the catalyst in quantities ranging from 1 to 50% by weight with respect to the total weight.

5. The process according to any of the previous claims, wherein the catalyst is used in the form of a finely subdivided powder, with an average diameter of the granules ranging from 10 to 250  $\mu\text{m}$ .

6. The process according to any of the previous claims, wherein the catalyst englobed in the paraffinic matrix is brought to a temperature which is greater than or equal to 150°C and diluted with a diluent liquid at those temperatures, and also at room temperature, until a concentration of solid ranging from 10 to 50% by weight, is obtained.

7. The process according to claim 6, wherein the diluent consists of an oligomer of  $\text{C}_6\text{-C}_{10}$   $\alpha$ -olefins.

8. The process according to any of the previous claims, wherein the pressure in the charging vessel (D) is higher than that present in the reactor (B) by about 0.2-0.4 MPa.

9. A process for the shut-down of a reactor (B) in which

reactions take place in multiphase systems according to the Fischer-Tropsch technology, wherein a gaseous phase, prevalently consisting of CO and H<sub>2</sub>, is bubbled into a suspension of a solid in the form of particles (catalyst) in a liquid (prevalently reaction product), which comprises the following operating phases:

- i. gradual stoppage of the feeding of synthesis gas (6) and its gradual substitution with inert gas (5);
- 10 ii. possible reduction of the operating pressure and temperature present inside the reactor (B);
- iii. discharging (4) of the suspension contained in the reactor (B) and in the units associated therewith (E), and its recovery in the vessel (A) heated and  
15 flushed with inert gas (3), wherein the transfer is effected by means of the difference in pressure, the vessel (A) having been previously brought to a pressure at least 3 bars lower than the reactor (B).

20 10. The process according to claim 9, wherein the vessel (A) is designed to have a capacity which is such as to contain the volume of suspension present in the reactor (B) and in the other units (E), associated with the treatment of the suspension, at the moment of shut-down.

25 11. A process for the running of a temporary shut-down

phase (stand-by) of a reactor (B) wherein reactions are effected which take place in multiphase systems according to the Fischer-Tropsch technology, wherein a gaseous phase, prevalently consisting of CO and H<sub>2</sub>, is bubbled into a suspension of a solid in the form of particles (catalyst) in a liquid (prevalently reaction product), which comprises:

1. gradual stoppage of the feeding of synthesis gas (6) and gradual substitution with inert and/or reducing gas (5) to keep the solid phase dispersed in the suspension;  
10
2. optional decrease in the operating temperature and pressure.
12. The process according to claim 11, wherein the reactor (B) is kept on-line with the treatment section of the suspension (E) which is completely recycled (11) and (12), to  
15 the reactor without the extraction of products.
13. The process according to claim 11, wherein the reactor (B) is taken off-line from the units (E) after emptying the suspension from the equipment (E) directly connected to the  
20 reactor (B).
14. The process according to claim 13, wherein the reactor (B) has a capacity which is such as to also contain the volume of suspension present in the units (E) at the moment of temporary shut-down.

25

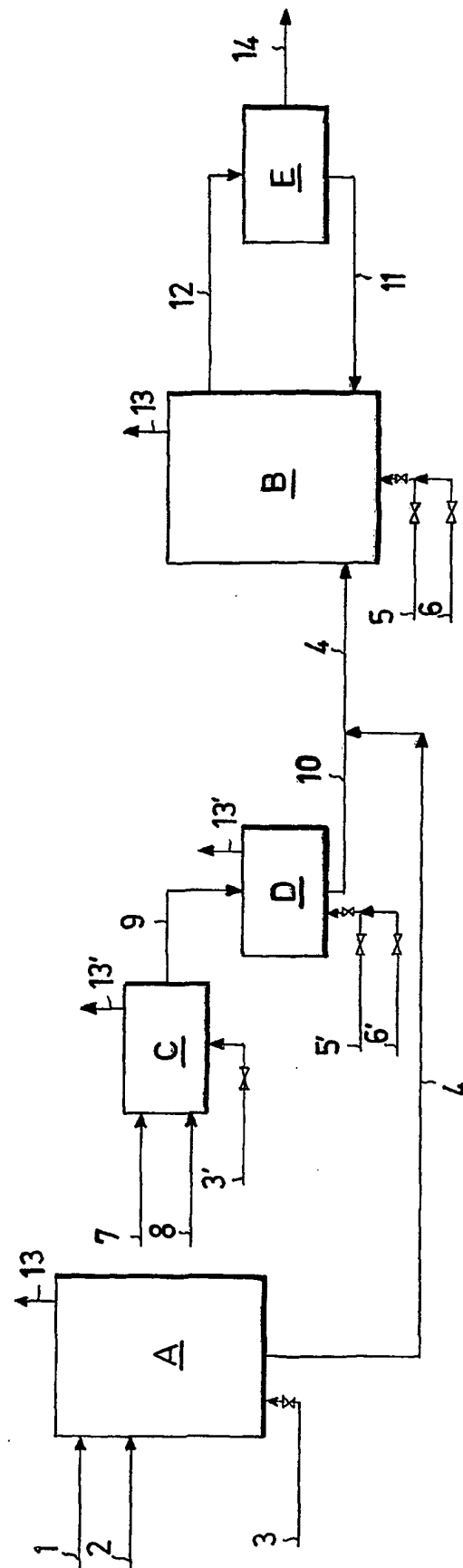



Fig. 1

# INTERNATIONAL SEARCH REPORT

International Application No  
 /EP2004/010635

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C10G2/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 03/068715 A (STEYNBERG ANDRE PETER ; SASOL TECH PTY LTD (ZA)) 21 August 2003 (2003-08-21) -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the International filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*&\* document member of the same patent family

Date of the actual completion of the international search

31 January 2005

Date of mailing of the international search report

07/02/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016


Authorized officer

Gilliquet, J-N

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

 EP2004/010635

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 03068715	A	21-08-2003	GB	2401112 A	03-11-2004
			WO	03068715 A1	21-08-2003

---